LA-UR -82-1064

Conf-820633--1

MASTER

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--82-1064

DE82 014072

TITLE: PREPARATION OF UO_2 FRAGMENTS FOR FUEL-DEBRIS EXPERIMENTS

AUTHOR(S): Marvin C. Tinkle
John A. Kircher
Renate M. Zinn
David T. Eash.

SUBMITTED TO 5th INTERNATIONAL MEETING OF MODERN CERAMICS TECHNOLOGIES
LIGNANO-SABBIADORO, Italy, June 14-19, 1982

Los Alamos Los Alamos National Laboratory

PREPARATION OF UO_2 FRAGMENTS FOR FUEL DEBRIS EXPERIMENTS.*

Marvin C. Tinkle, John A. Kircher, Renate M. Zinn, and David T. Eash,
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

ABSTRACT

A unique process was developed for preparing multi-kilogram quantities of > 90% dense fragments of enriched and depleted UO_2 sized 20 mm to 0.038 mm for fuel debris experiments. Precipitates of $UO_4 \cdot xH_2O$ were treated to obtain UO_2 powders that would yield large cohesive green pieces when isostatically pressed to 206 MPa. The pressed pieces were crushed into fragments that were about 30% oversized, and heated to 1800°C for 24 h in H_2. Oversizing compensates for shrinkage during densification. Effort was dramatically reduced by working on a large scale and by presizing the green UO_2 instead of directly crushing densified pellets.

INTRODUCTION

This paper describes a method of preparation for UO_2 fragments of >90% of theoretical density. They were needed for experiments carried out by Sandia National Laboratories, to provide information necessary for post-accident heat removal analysis of sodium-cooled reactors. The requirements were that the fragments be made with both enriched and depleted UO_2, have a specific size range distribution and be of closely controlled density, purity, and stoichiometry.

We realized that crushing densified pellets into the proper sizes would be very laborious and inefficient. Therefore we developed a process in which ceramic UO_2 powder could be isostatically pressed into large (1 to 2 kg) logs which could be broken up fairly easily into green fragments of UO_2 for subsequent densification.

METHODS

U_3O_8 was dissolved in HNO_3 and the resulting uranyl nitrate solution, with a molarity from 0.6 to 1.0, was clarified by filtration. Then a quantitative precipitate of $UO_4 \cdot xH_2O$ was obtained by the simultaneous addition of 30% H_2O_2 and concentrated NH_4OH at a constant pH of 2.0. NH_4OH is used to neutralize HNO_3, which is a side product, in order to maintain a constant pH. Malonic acid at 0.2 M was added as a flocculent together with 0.02 M

*Work performed under the auspices of the US Nuclear Regulatory Commission

citric acid, which complexed iron and prevented the decomposition of H_2O_2 (ref. 1). The precipitated $UO_4 \cdot xH_2O$ was separated by vacuum filtration and placed into platinum boats.

The chemical equations for this method are as follows:

$$2U_3O_8 + 14HNO_3 \xrightarrow{\Delta} 6UO_2(NO_3)_2 + N_2O_3 + 7H_2O \quad (1)$$

$$UO_2(NO_3)_2 + H_2O_2 + xH_2O \rightarrow UO_4 \cdot xH_2O + 2HNO_3 \quad (2)$$

The enriched $UO_4 \cdot xH_2O$ was made by a continuous, automated precipitator system, designed to assure nuclear criticality safety. The uranium feed and the precipitants were delivered through rotameters at rates which assured a 20% excess of H_2O_2 relative to uranyl nitrate. Using a glass-calomel electrode pair and an automatic titrator, the pH in the precipitation vessel was maintained at 2.0 by addition of concentrated NH_4OH on demand. The slurry formed in the precipitation vessel was continuously stirred. The slurry was allowed to overflow through tubing to another vessel which provided additional contact time between the reactants; this vessel, called the digester, also has continuous stirring. The slurry then overflowed from the digester to a vacuum drum filter. The wet $UO_4 \cdot xH_2O$ cake was scraped from the surface of the drum by a doctor blade into platinum boats. (See Fig. 1.).

In contrast, the depleted $UO_4 \cdot xH_2O$ was made in separate batches of 500 g each; clarification, precipitation, vacuum filtration of the precipitate in Buchner funnels, and transferral to platinum boats were all done by hand.

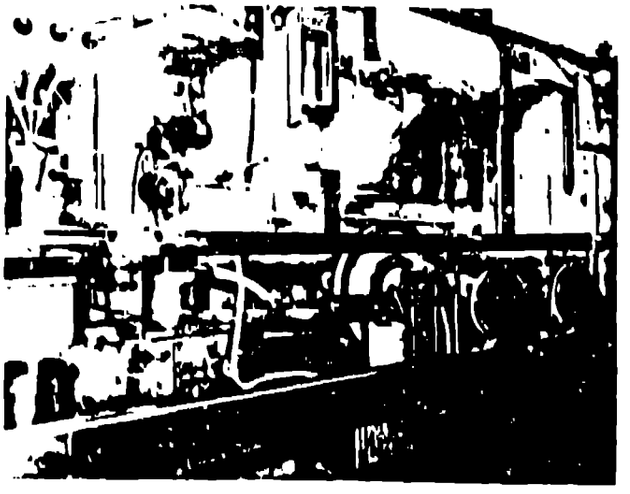

Fig. 1. Continuous precipitation system and drum filter.

The $UO_4 \cdot xH_2O$ was calcined at 300°C for 8 hours to a composition approximating UO_3. In order to obtain a highly sinterable UO_2 from the UO_3, the following steps were carried out on 1-kg batches in 5-in.-diameter reactors: (1) the UO_3 was reduced to UO_2 at 650°C for one hour in flowing H_2 at 4 ℓ/min; (2) the resulting UO_2 was oxidized in air for 6 h at 350°C; and (3) the oxidized material was re-reduced to UO_2 under the conditions of step (1). Oxidation and re-reduction of the UO_2 breaks up agglomerates in the powder. Immediately following this second reduction, the oxide was treated at 650°C in a flow of 2 ℓ/min of helium and 250 g/h of H_2O vapor. The water vapor is introduced by bubbling helium through a flask of water held near the boiling point, and is then carried through the preheater tube that runs the length of the reactor. This treatment slightly oxidizes the UO_2 to a composition of about $UO_{2.1}$, which can easily be handled in air without burning.

The UO_2 was passed through a 0.6 mm sieve to obtain a flowable powder and was sealed into plastic bags for pressing. The bags were about 7 cm in diameter by 30 cm long, with walls of 2 mm thickness. The filled bags were isostatically pressed to 206 MPa (30,000 psi). (See Fig. 2, which shows the isostatically pressed UO_2 before and after removal of the log from the plastic bag, and the mode of fracture of the log.) The resulting pressed logs were crushed into fragments and sieved to sizes that were about 30% larger than the required finished sizes, to compensate for shrinkage during the subsequent sintering step.

The oversized fragments were loaded into molybdenum boats in amounts of 5 kg each and heated at 1800°C for 24 h in a Harper molybdenum-wound, alumina-

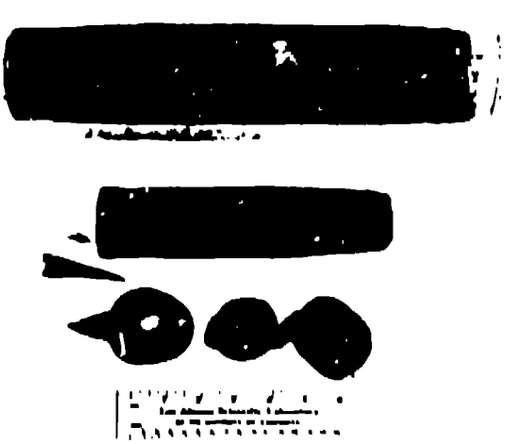

Fig. 2. Isostatically pressed UO_2.

refractory hydrogen atmosphere furnace. A stainless-steel transfer box, which is purged with argon, is used to load and unload the boat while the furnace is at 1000°C. (See Fig. 3.) In a run, the boat is moved from the transfer box into the coldest part of the furnace chamber and then in stages into the hottest zone. The temperature of the furnace is next increased at about 100°C/h to 1800°C. After the UO_2 has been heated in hydrogen at 1800°C for 24 h, the boat is moved in stages to the coldest part of the furnace chamber and the furnace is allowed to cool to 1000°C. At that point the boat, which is below red heat, is moved into the transfer box to cool to room temperature in a flow of argon.

The densified fragments stuck together very little and could be separated by lightly crushing with a mortar and pestle. They were then sieved to size fractions ranging from 4-20 mm down to 0.038-0.045 mm. (The required intermediate size fractions were obtained using every other sieve size in the U.S.A. Standard Series.) Figure 4 shows densified fragments in the 4-20 mm range.

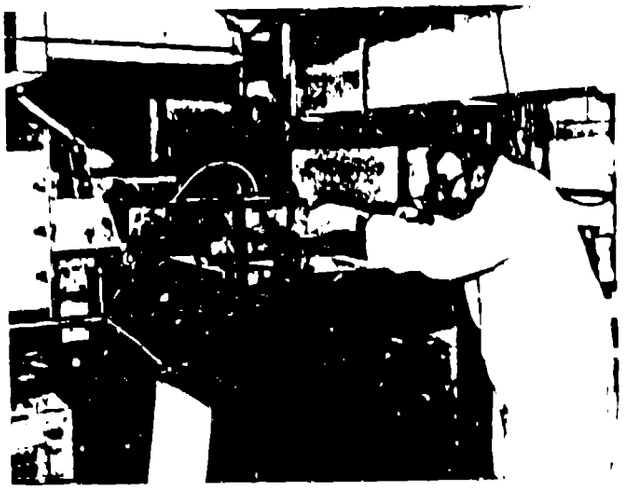

Fig. 3. Hydrogen atmosphere furnace with transfer box.

RESULTS AND DISCUSSION

Eighty kilograms of dense UO_2 fragments were produced for fuel debris experiments. Some process development was done during the actual production. For example, a more easily prepared UO_2 powder was tried, but it required isostatic pressing at 309 MPa (45,000 psi) to produce green fragments that could be sintered to >90% of theoretical UO_2 density at 1800°C, the operational limit of the hydrogen furnace. Also, crushing of those logs produced a large

Fig. 4. UO_2 fragments, 4-20 mm.

amount of fines, which was unacceptable because of the amount of recycle required for the enriched uranium. The selected process described above is the one that had the best overall efficiency for accomplishing the task.

Particle density measurements by mercury porosimetry on dense UO_2 fragments made by the selected process yielded values that were close to 95% of the theoretical density of UO_2. The density values determined by mercury intrusion at 15,000 psi were only a few tenths of a percent higher than those obtained at 100 psi, indicating that the particles had very little interconnected porosity. This was consistent with the appearance of polished sections of the particles in metallographic mounts which had been prepared by pressure impregnation of epoxy resin at 1000 psi.

Metallographic examination of polished sections of the final particles strongly indicated high sinterability at 1800°C in hydrogen of the compacted UO_2 in the green fragments; the grain size was quite large (up to about 25 μm). This suggests that it might have been possible to achieve the target density of >90% of theoretical by heating in hydrogen at a temperature lower than 1600°C.

The final particles were stoichiometric UO_2 of high purity. Ratios of O/U up to only 2.01 were obtained by calculation from uranium analyses. X-ray diffraction analyses confirmed that the ratios were no higher than 2.01 based on lattice parameters (ref. 2,3) between 5.47098 Å and 5.47118 Å with uncertainties in the range from ± 0.00007 Å to ± 0.00015 Å. The high purity of the dense UO_2 particles is shown by the data in Table 1.

TABLE 1

Typical spectrochemical analysis

Elements	ppm	Elements	ppm
Li	<0.2	Fe	~75
Be	<0.2	Ni	<5
B	<0.2	Cu	3
Na	<1	Zn	<25
Mg	1	Sr	<40
Al	~15	Mo	<25
Si	5	Ag	<1
P	<100	Cd	<2
Ca	<5	Sn	<1
V	<25	Sb	<5
Cr	<1	Ba	<5
Mn	<1	Pb	<2

CONCLUSIONS

Multi-kilogram quantities of >90% dense fragments of enriched and depleted UO_2 with particle sizes from 20 mm to 0.038 mm can be readily prepared by a process that involves (1) precipitation of $UO_4 \cdot xH_2O$ from uranyl nitrate solution, (2) preparation of compactable UO_2 by simple gas-solid reactions, (3) isostatic pressing of the UO_2 into 1-2 kg logs that are coherent but easily broken up into fragments of appropriate size, and (4) sintering the fragments in hydrogen at 1800°C. The fragments produced in large quantities in this way are comparable to those obtained by crushing sintered, dense UO_2 pellets, and are much cheaper to prepare.

ACKNOWLEDGEMENTS

The authors wish to thank J. A. O'Rourke for x-ray determination of lattice parameters and R. D. Reiswig for determination of grain size by metallographic sections. We are indebted to D. J. Sasmor of Sandia National Laboratories for his helpful comments.

REFERENCES

1. B. L. Kelchner, Qualitative Survey of the Physical Factors Affecting the Precipitation of Uranium from Uranyl Nitrate Solution with H_2O_2, Los Alamos Scientific Laboratory report LA-1069, July 7, 1950.
2. J. Belle (Ed.), Uranium Dioxide. Properties and Nuclear Applications, USAEC, pp 233-236.
3. P. J. Baldock, W. E. Spindler, and T. W. Baker, The X-Ray Thermal Expansion of Near-Stoichiometric UO_2, J. Nucl. Mat. 18, (1966) 305-313.